Dissolution Dynamics of Chemically Amplified Resists for Extreme Ultraviolet Lithography Studied by Quartz Crystal Microbalance

Masaki Mitsuyasu, Hiroki Yamamoto, Takahiro Kozawa

The Institute of Scientific and Industrial Research, Osaka University,
8-1 Mihogaoka, Ibaraki,Osaka 567-0047, Japan

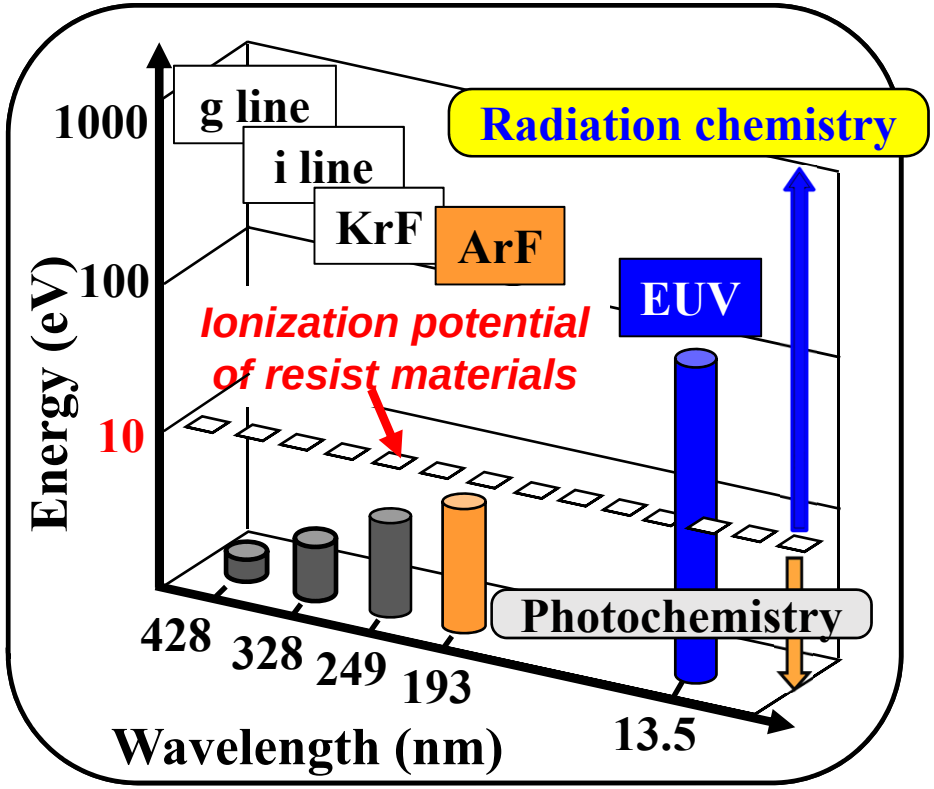
Introduction

Lithography roadmap

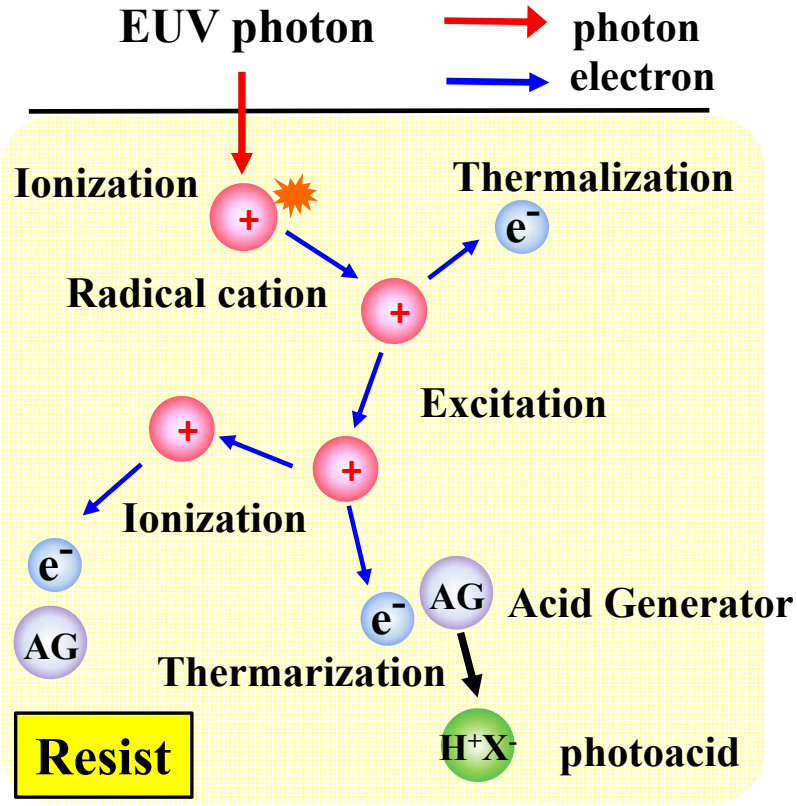
Year of production	2015	2016	2017	2018	2019	2020
Line pattern size	24 nm	22 nm	20 nm	18 nm	17 nm	15 nm
Exposure source	ArF (193 nm)		Extreme ultraviolet (13.5 nm)			

(ITRS2013)

Ionization potential of resist material



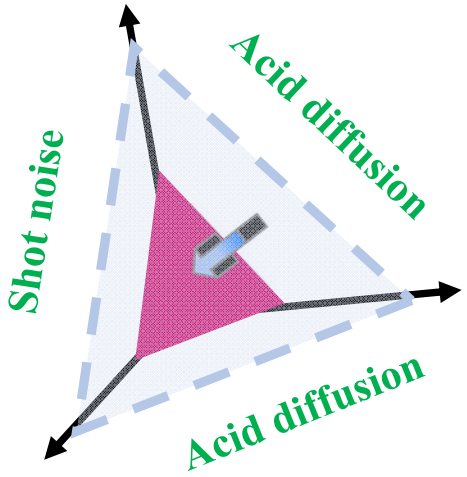
Energy deposition of EUV photons



Introduction

Specification of DRAM $^1/_2$ pitch = 16 nm

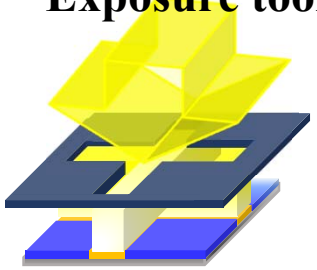
Sensitivity (5-15 mJ/cm^2)



LER (3 σ = 0.9 nm)

Resolution (16 nm)

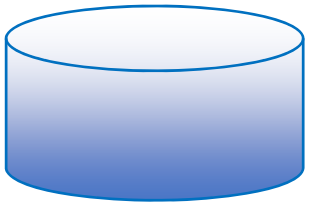
Exposure tool



Accumulated energy profile

Latent acid image

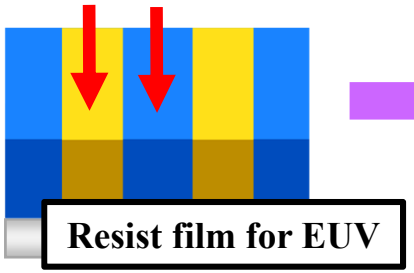
Acid catalyzed image



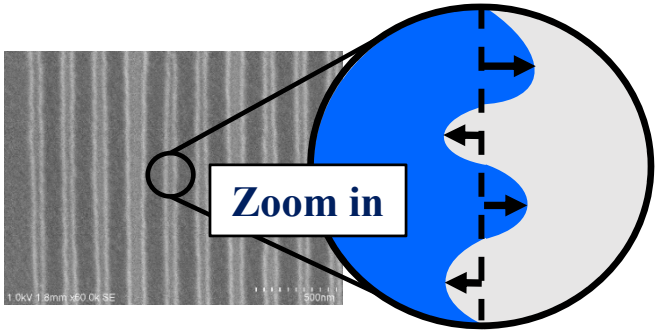
Development

Development

Dissolution contrast

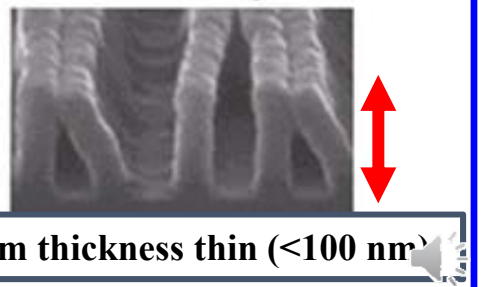


LER



or

Pattern collapse



Effect of Low-Molecular Weight Resist Components

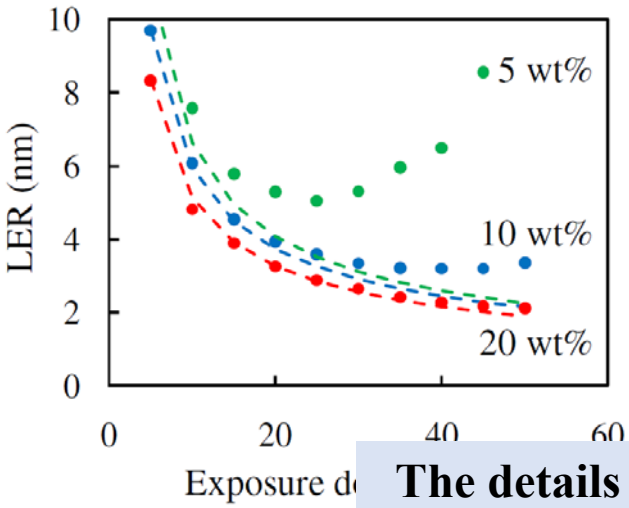
Acid concentration (TPS-tf)	5	10	20
Abs. Coefficient	3.8±0.2	3.8±0.2	3.8±0.2
Quantum efficiency	1.7	2.5	3.1

Quantum efficiency increases with increase in acid generator concentration

Hirose et al. Jpn, J. Appl. Phys., **46**. No. 40, 2007.

Acid generator concentration

Simulation

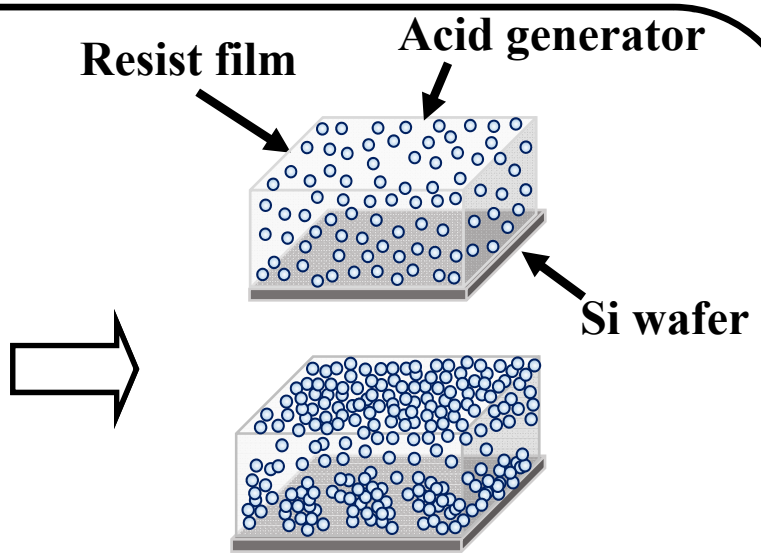


T. Kozawa. *Jpn. J. Appl*

Increase

LER

Sensitivity

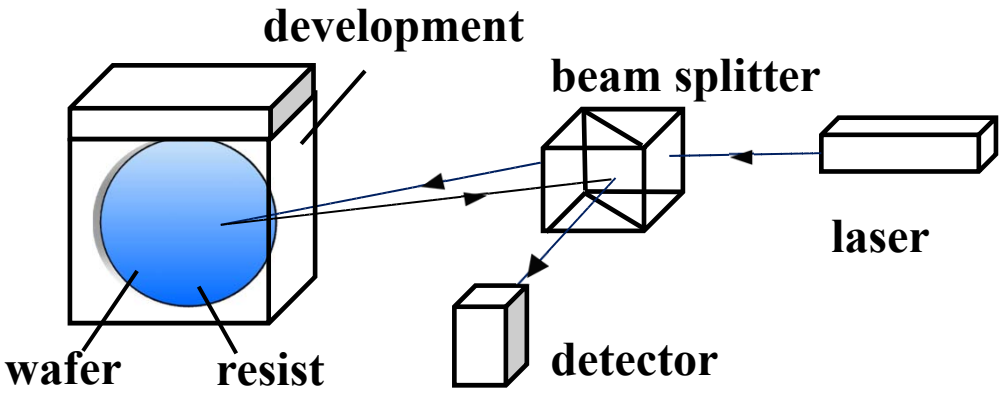


With the increase in acid generator concentration of erator increses.

The details in the effects of low-molecular weight resist components should be investigated.

Measurement of Dissolution Behavior of Resist Film

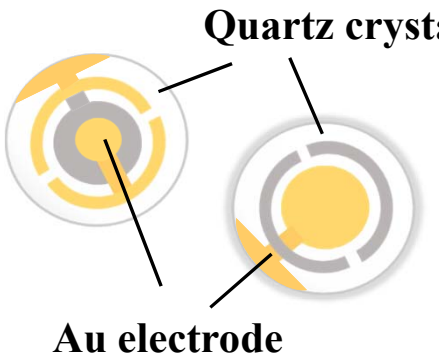
Optical interference method

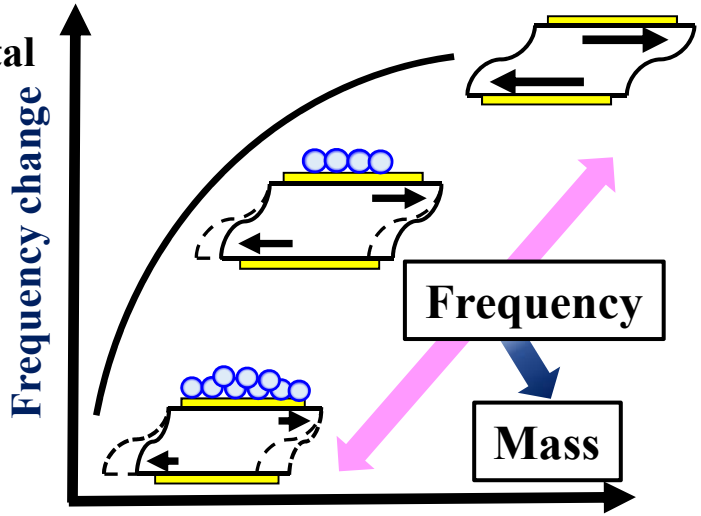


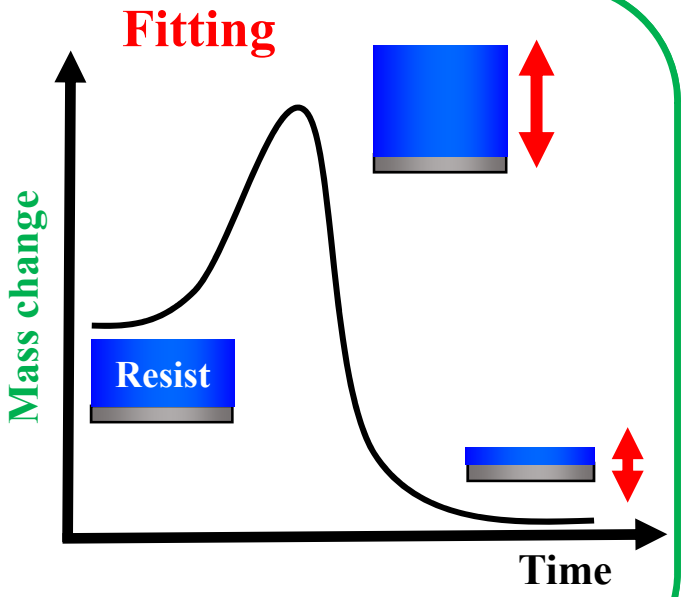
Pattern collapse

Film thickness thin (<100 nm)

Quartz crystal microbalance (QCM) method





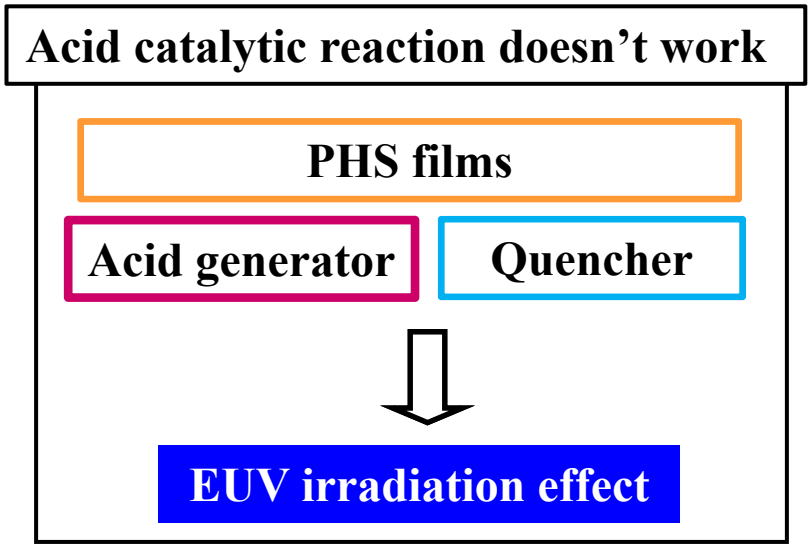


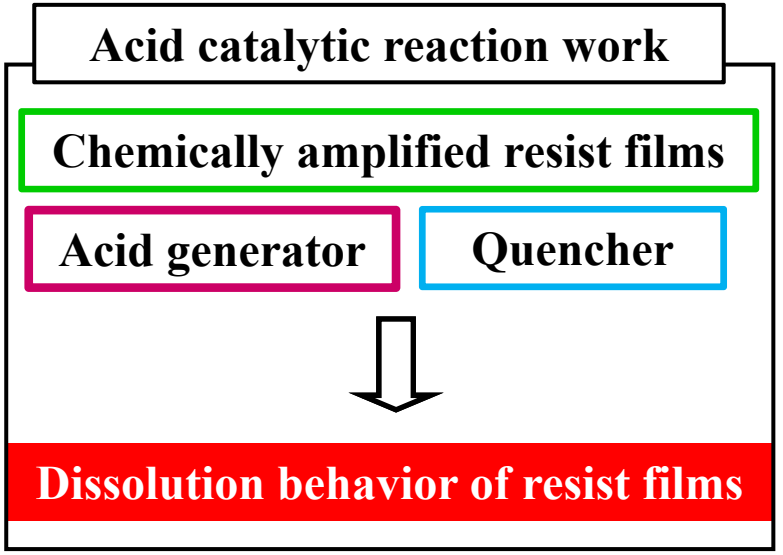
W. Hinsberg, et al. J. Electrochem. Soc. **133** 1448-1451(1986)

We can measure the change of film thickness less than 100nm.

Objective

To understand the effect of each resist components on dissolution behavior, the dissolution dynamics of chemically amplified resist after EUV exposures was investigated.

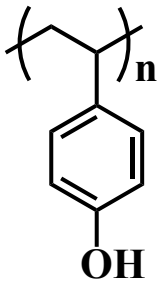




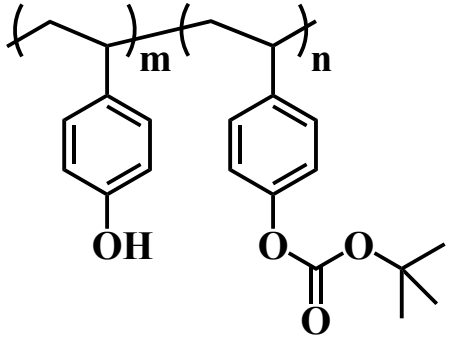
The dissolution behavior of resist film with less than 100 nm was investigated from the standpoint of a systematic understanding of resist dissolution.

Samples

Polymer

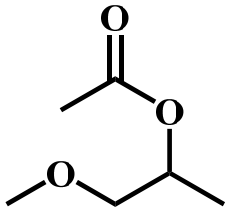


PHS
poly(4-hydroxystyrene)
Mw : 11000



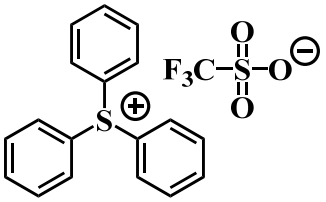
***t*BOC-PHS**
poly(4-hydroxyl-*co*-*t*-butoxycarbonyloxy)styrene
Mw : 10400, protecting ratio : 30.7%

Solvent

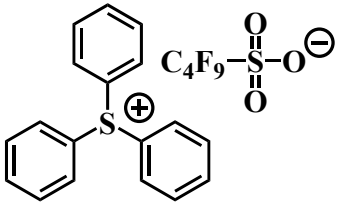


PGMEA
(propylene glycol monomethyl ether acetate)

Photoacid generator (PAG)

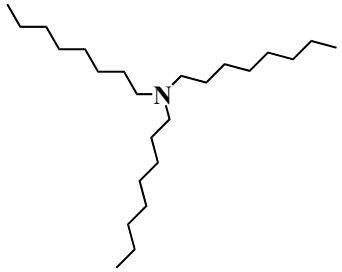


TPS-tf
(triphenylsulfonium triflate)



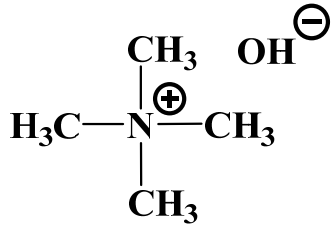
TPS-nf
(triphenylsulfonium nonaflate)

Quencher



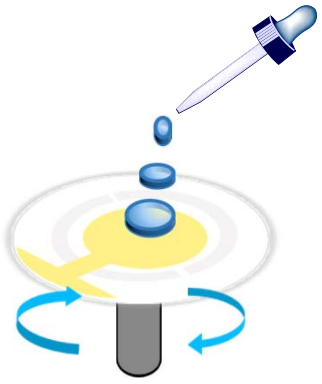
TOA
(trioctylamine)

Development



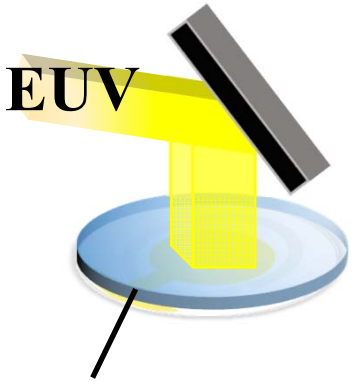
TMAH
(tetramethylammonium hydroxide)
2.38% aqueous solution

Experimental



Spin-coating

Bake
(90°C, 90 sec)

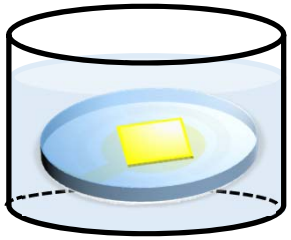


c. a. 100 nm

EUV exposure

(EQ-10M, Energetic)

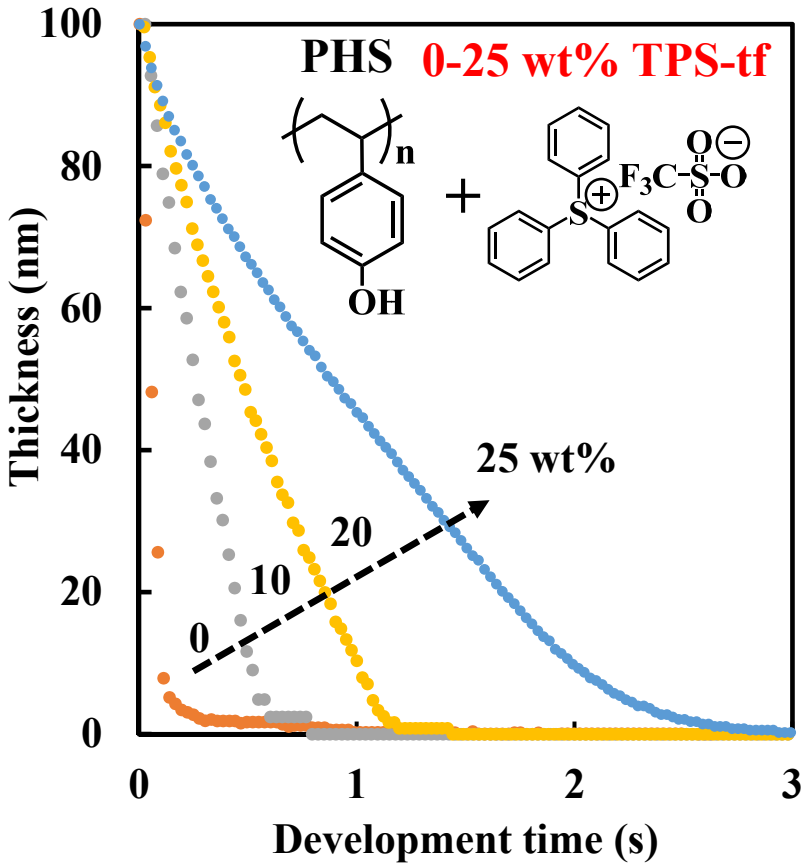
Post exposure bake
(90 °C, 60 sec)



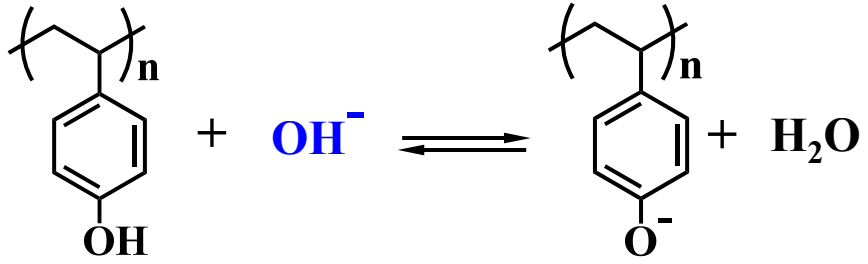
Development

Result / Dependence on PAG concentration

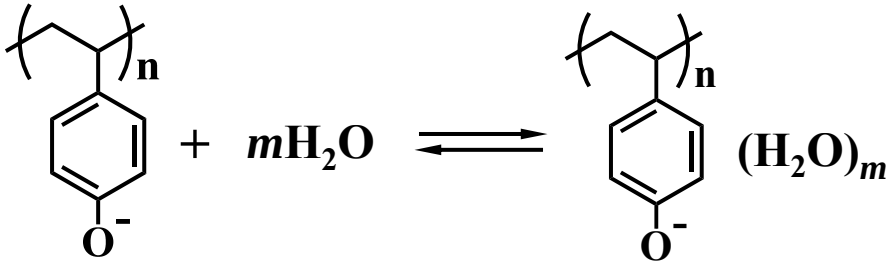
Unexposed films



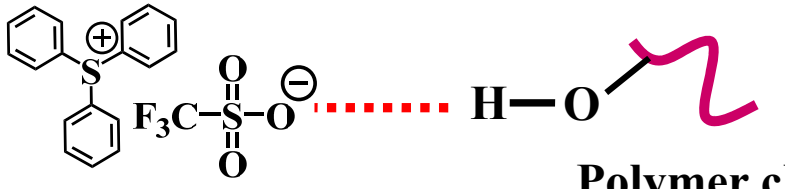
Deprotonation



Solvation

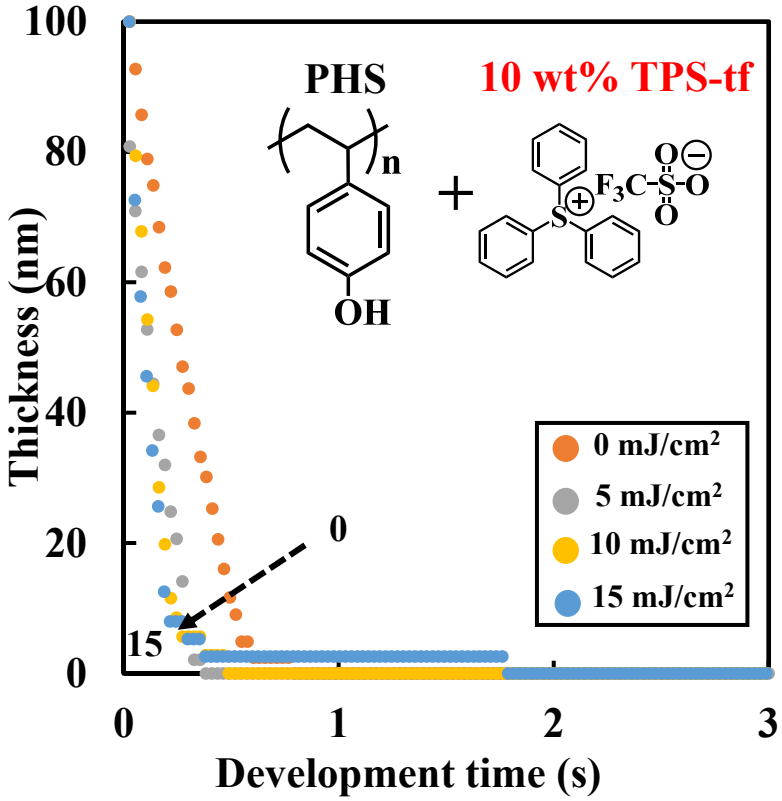


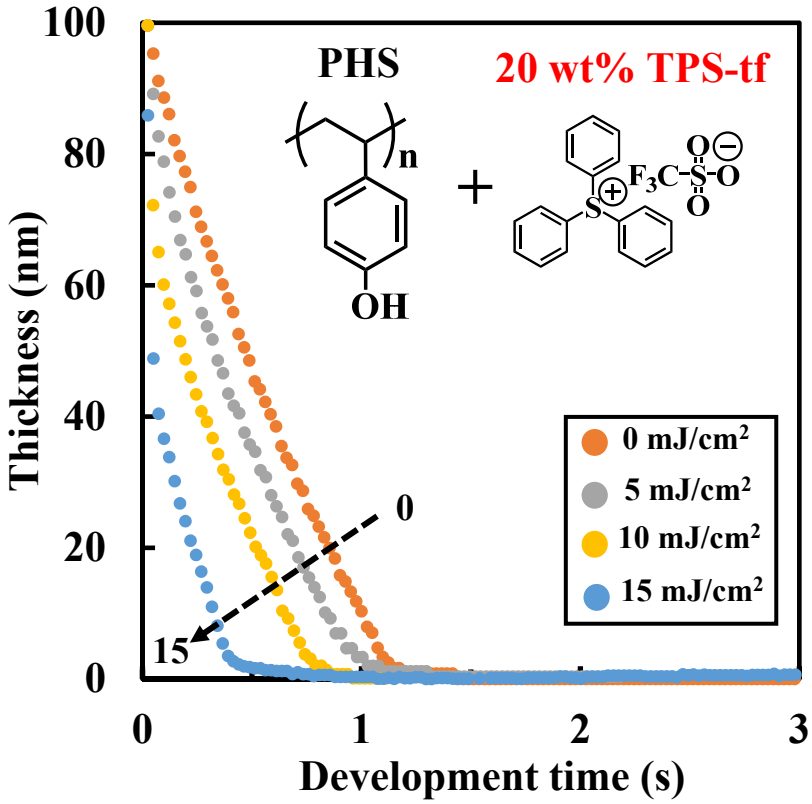
Interaction

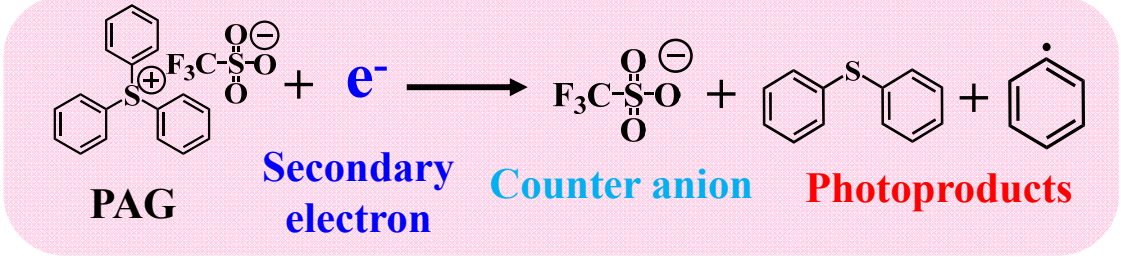


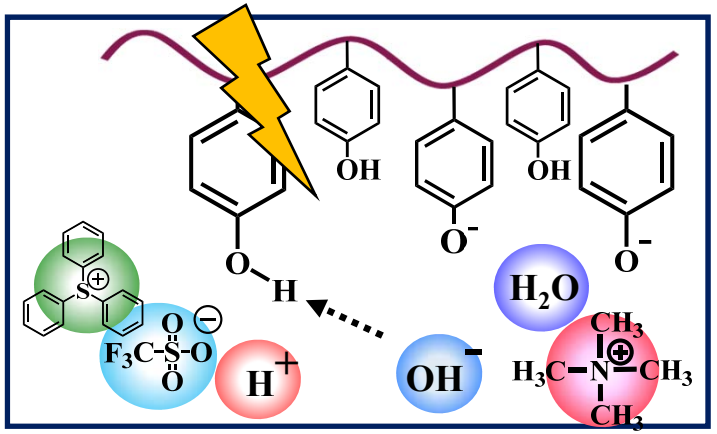
Z. Yan. et all *Macromolecules*. ***31***, *1998, 7723-7727*

Result / Dependence on Exposure Dose



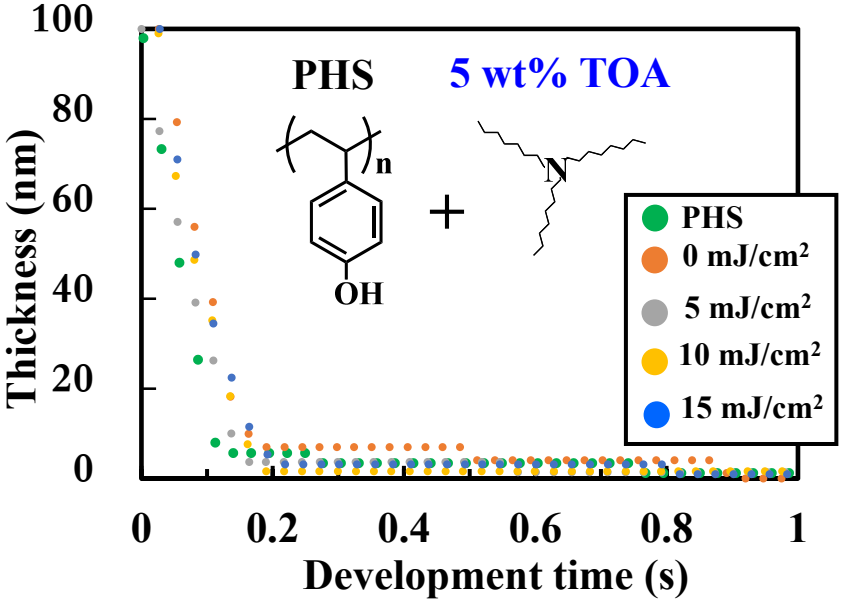


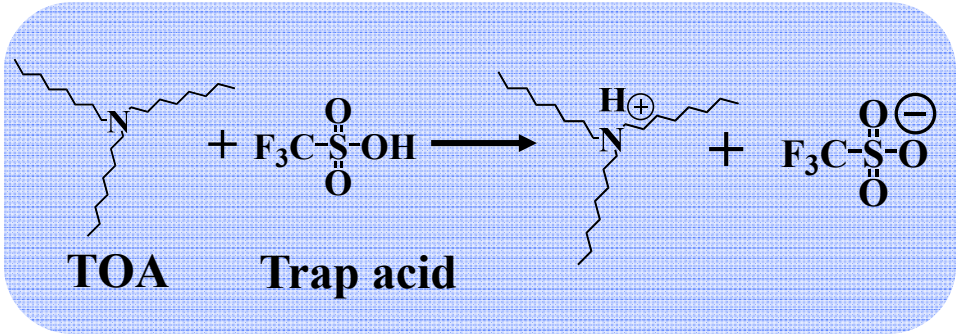


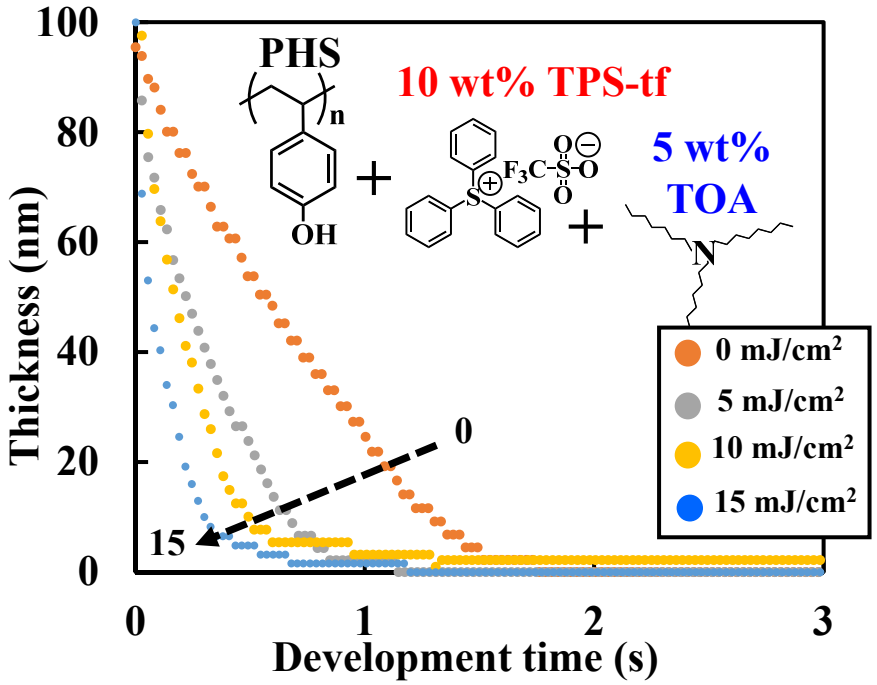


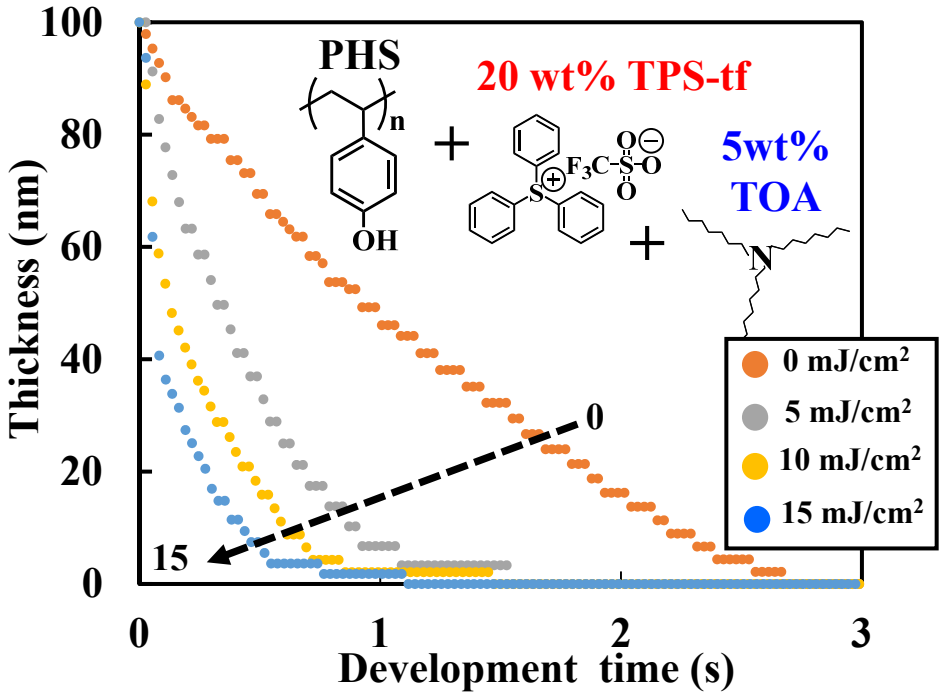
Acid generator is decomposed by EUV exposure, and counter anion is generated

Result / Quencher and PAG



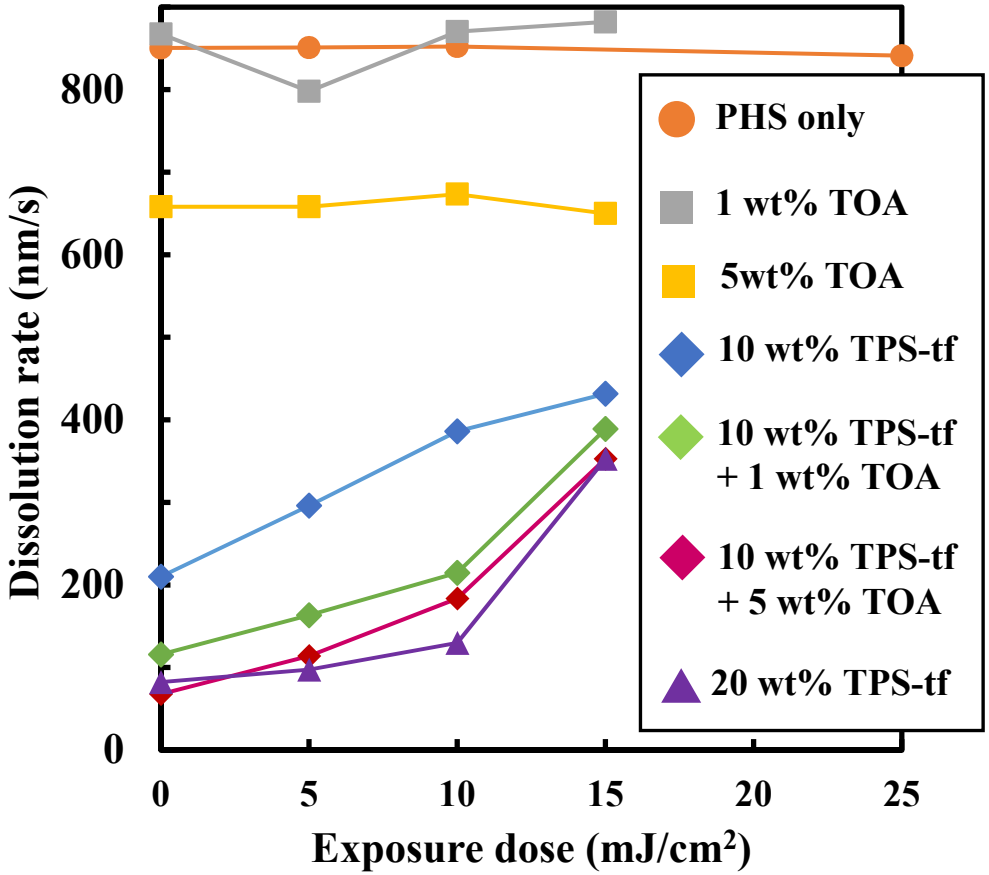






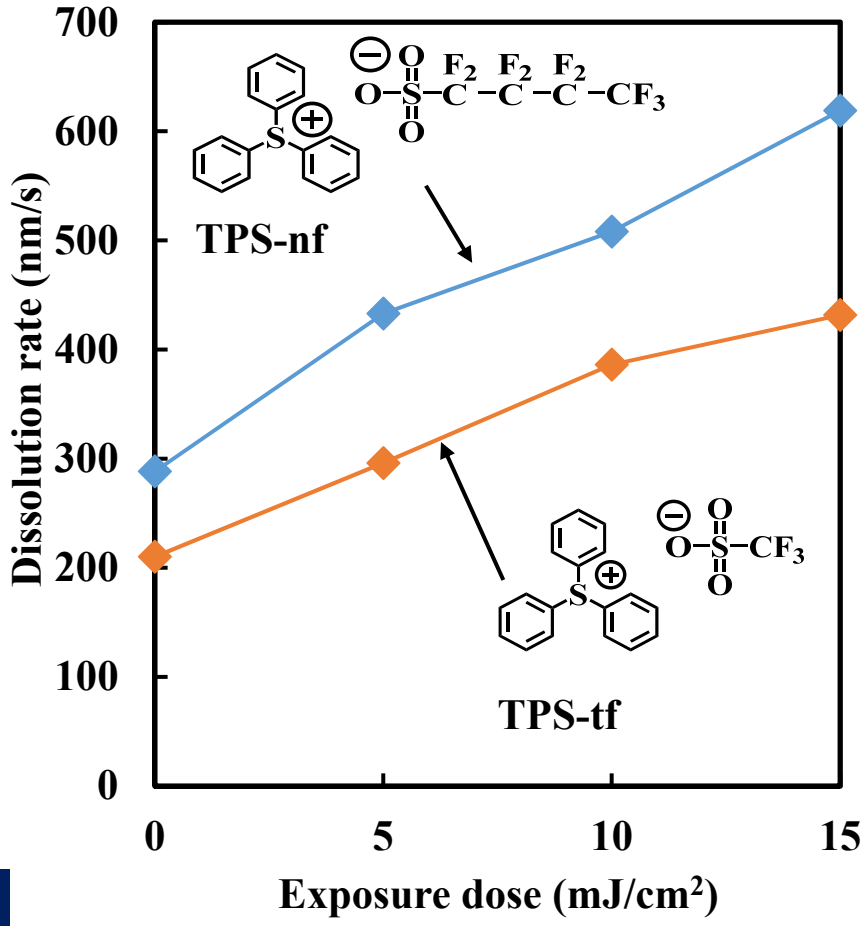
Result / Dissolution Rate

Effects of resist components on dissolution rate



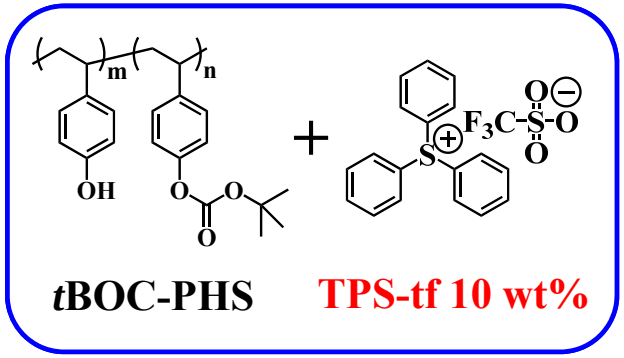
- Some resist components have the inhibition effect on dissolution.
- The solubility in the developer depends on the remaining acid generator.

Effects of anions

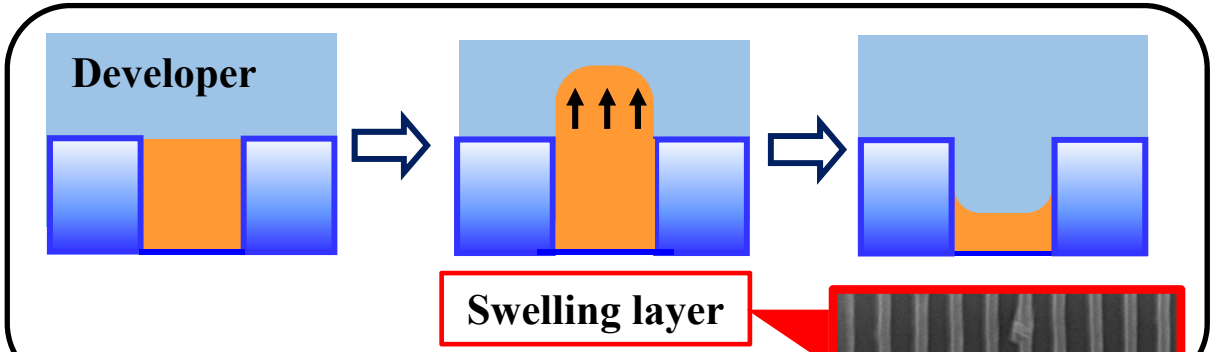


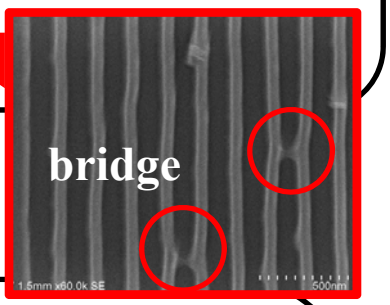
TPS-nf is faster than TPS-tf

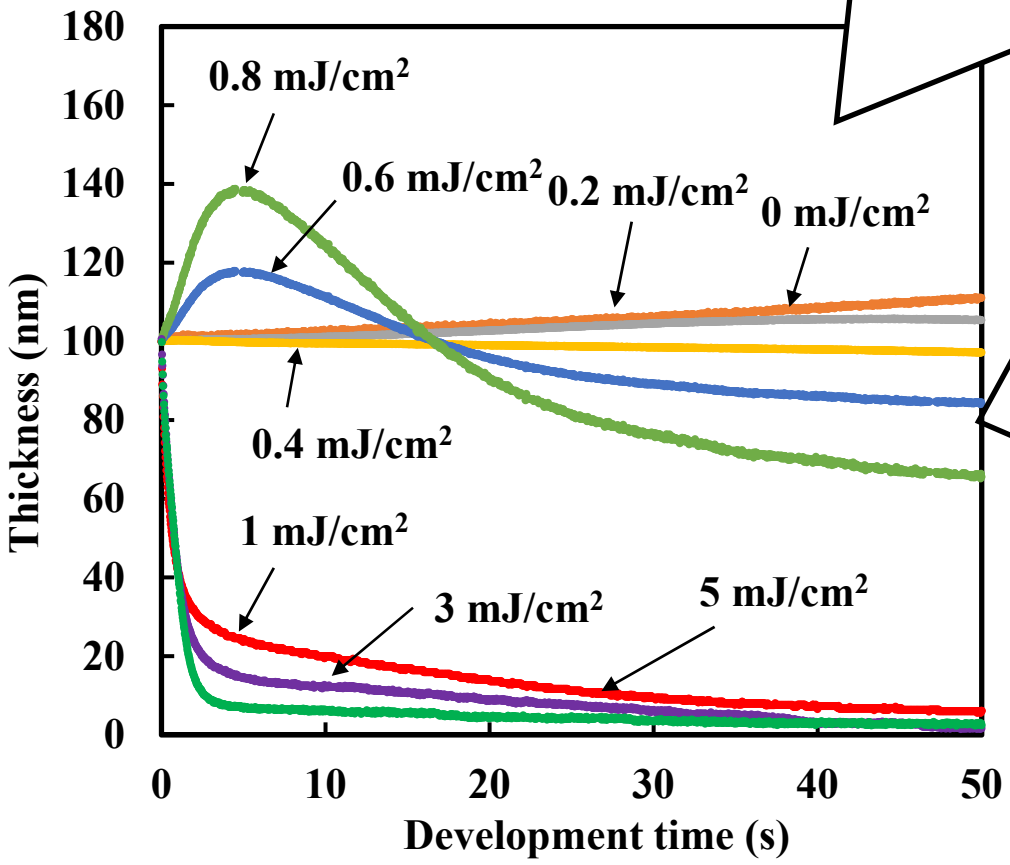
Result / Dissolution behavior of *t*BOC films

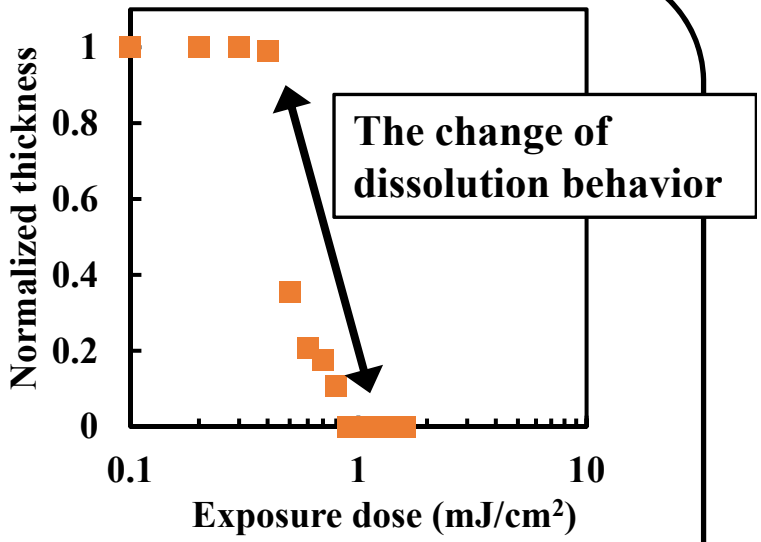


*t*BOC-PHS TPS-tf 10 wt%









- The sensitivity is 0.8-1.0 mJ/cm²

Conclusion

- The dissolution behavior of less than 100 nm resist films was investigated from the standpoint of a systematic understanding of the effects of each resist component on dissolution using QCM.
- The solubility in the developer depends on the remaining PAG concentration and the structure of acid generators.
- In *t*BOC-PHS films, the swelling of resist film containing 10 wt% TPS-tf was observed before and after EUV exposure.
- The dissolution speed became slower with increase of TPS-tf concentration in PHS and tBOC-PHS. It is important for the EUV resist design to take into account the concentration of undecomposed PAG.

Acknowledgment

We are grateful to Tokyo Ohka Kogyo Co. Ltd. for supplying the polymer.

Thank you for your kind attention